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## (54) OPTICAL ELEMENT FORMED OF LOW ABSORBING MATERIAL FOR RECORDING AND MANUFACTURING PROCESS OF THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an optical element for recording formed of a substrate and an optical recording layer and a light reflecting layer formed on the substrate.

SOLUTION: An optical recording layer 12 has a material expressed by  $\text{TeaGebCcHdOe}$ . Here, a, b, c, d and e indicate atomic percentage satisfying the following relations;  $(c+d)>40$ ,  $d>10$ ,  $a>5$ ,  $b>b$ ,  $e\geq 0$  and  $a+b+c+d+e=100$ . Moreover, the reflection layer 14 and optical recording layer 12 are selected to the elements  $R_{\min}$  or  $R_{\max}$  (element reflectivities) of have about 70% or more at about 780nm.



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CLAIMS

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[Claim(s)]

[Claim 1] Including a substrate, it has an optical recording layer and a light reflection layer in order on the surface, and an optical recording layer has at least two sublayers of a different presentation.;

b) A recordable element chosen so that thickness of an optical recording layer and a reflecting layer may be more than about 70% or it to a laser wavelength whose  $R_{\min}$  reflectance of an element is about 780 nm.

[Claim 2] Including a substrate, it has a recording layer and a light reflection layer in order on the surface, and is a. A recording layer has the presentation of material which changes along a thickness direction.;

b) A recordable element whose inclination and thickness of a presentation of a recording layer and a reflecting layer are more than about 70% or it to a laser wavelength whose  $R_{\min}$  reflectance of an element is about 780 nm.

[Claim 3] An optical recording layer is provided by carrying out sputtering of the two sublayers of a different presentation like characterized by comprising the following.;

A substrate is included and it is an optical recording layer to order on the surface.

having a light reflection layer -- a -- the thermal and optical characteristic that each of them differs.

b) A process of manufacturing a recordable element which consists of each stage which forms thickness of an optical recording layer and a reflecting layer to a laser wavelength whose  $R_{\min}$  reflectance of an element is about 780 nm so that it may be more than about 70% or it.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]U.S. patent applications 08/399787 "Recordable Optical Element Using Low Absorption Materials" for which it applied on March 7, 1995 by the cross-reference Tyan of related application, etc. are referred to.

[0002]

[Field of the Invention]This invention relates to the above-mentioned element useful as a recordable compact disk, concerning an optical record element.

[0003]

[Description of the Prior Art]Many molds are among the optical information support elements known. The gestalt good [ including optical information ] and used is a compact disk or CD. If digital information is not so, it will be memorized in the mark of the low reflectance on the reflexible background, or the form of a pit. The strict specification of CD format is published by Sony and Philips, and these formats are used as a standard all over the world. One of the most important format demands is the reflectance of the background decided to be larger than 70% at about 780 nm. This high reflectivity value is not usual compared with other optical recording disks. In order to write in in order that reflectance may make an ordinary information record process easy in the case of the latter, and to improve absorption of laser energy, it is designed low.

[0004]At CD, optical information has most forms of read-only memory or ROM. Light information is rather manufactured with a press by a mold rather than is usually recorded in real time. In a typical process, a recording substrate is the first mass manufactured by the press mold using a stamper including the digital information reproduced. The substrate by which the press mold was carried out is a reflecting layer, and then overcoat is carried out by an optical protective layer. In these fields that have modification or a pit, reflectance is lower than a field without modification.

[0005]It can record in real time and to manufacture the optical record element which can make the record which copies the conventional CD by reading is desired. Thus, information is recorded on CD, and CD is read over by the conventional CD reproduction machine, and it deals in it. The recorded element had to suit the strict specification of CD, therefore was difficult to manufacture such an optical record element. It was difficult to manufacture the recordable element which suits especially >70% reflectance.

[0006]One method of manufacturing the recordable element imitating the conventional mold press CD element is providing the transparent base material which has a layer which absorbs record radiation in order on it, and a reflexible layer and which can carry out heat modification. When it emanates through a transparent base material, reflectance changes with the thickness of an absorption layer as a result of the cross protection of light (drawing 1). When the absorption layer of very small thickness (much smaller than corresponding to  $R_{\min}$ ) is used, reflectance is high, but such a structure is not useful to the purpose of record of low thermal efficiency therefore. A reflecting layer is a very efficient heat sink. Most writing energies absorbed by the next of the reflector of an optical recording layer are conducted by a reflector, and it dissipates. The minimum useful thickness is a thing made from reflection with the reflectance near the first minimum. Therefore, in order to manufacture a useful record element, the material which has >70% of reflectance by bigger thickness than the useful thickness of this minimum is required. Such a material is characterized with a low optical absorbance coefficient the material and the contrary which are used for the conventional record structure which needs high optical absorbance. Generally these low absorbent materials do not demonstrate good performance, when used without a reflector with the conventional medium structure. Suitable sensitivity and contrast can be attained only when incorporated in a perfect optical interference structure of using a reflector. Thus, generally a suitable material for the conventional record structural steel worker is not suitable to recordable CD structure, and reverse is also truth.

[0007]It applies [ U.S. Pat. No. 4940618 and European Patent ] No. 0353393, and this type based on organic coloring matter of material is indicated to Canadian patent No. 2005520. One of the features which are not desirable as for the element based on such organic coloring matter is the wavelength sensitivity. The desirable optical characteristic is obtained and sold only at the wavelength near the absorption edge of such coloring matter. It depends for the reflectance and other characteristics of such an element on wavelength strongly as a result. It is dramatically difficult to suit the specification of all the severe CDs through the whole range of the wavelength designed so that CD may function. Since storage density is increased, it is next to impossible to operate such an element using short wavelength than being used with a future generation's CD.

[0008]However, U.S. patent applications 08/399787 of March 7, 1995 application contain a

certain non-coloring matter medium with which it is satisfied of reflectance characteristic of CD. One of the faults of such a non-coloring matter medium is those comparatively low low-temperature efficiency. The power demanded in order to write in by perfect contrast is notably larger than being required from the record element based on coloring matter.

[0009]

[Problem(s) to be Solved by the Invention]While the purpose of this invention follows CD specification, there is in providing the improved record element which can operate in notably high recording sensitivity and the wide wavelength range.

[0010]

[Means for Solving the Problem]Including a substrate, the above-mentioned purpose has an optical recording layer and a light reflection layer in order on the surface, and is a. An optical recording layer has at least two sublayers of a different presentation.;

b) Thickness of an optical recording layer and a reflecting layer is attained by recordable element chosen to a laser wavelength whose  $R_{\min}$  reflectance of an element is about 780 nm so that it might be more than about 70% or it.

[0011]

[Embodiment of the Invention]It is the important feature of this invention to be chosen so that it may be more than about 70% or it, as the reflecting layer 14 and the optical recording layer 12 of this element fills [ element  $R_{\min}$  or  $R_{\max}$  (reflectance of an element) ] CD specification. Term  $R_{\min}$  and  $R_{\max}$  are well known for this technical field. The illustration curve of reflectance versus [ to the typical optical element which has a reflective pair in the wavelength of arbitrary lights ] thickness is shown in drawing 1. The unit of thickness is arbitrary. A curve is a thing which represents all the materials which return to the maximum called  $R_{\max}$  by the optical interference which reflectance leaves a high value, and descends to the minimum called  $R_{\min}$  by the optical interference negated mutually next, and is reinforced mutually.  $R_{\max}$  is always larger than  $R_{\min}$  so that it may be shown to any given optical elements. Although thickness was usually chosen by  $R_{\max}$  with the optical element, it became clear that thickness was  $R_{\min}$  or near it and it obtained by this invention. With reference to drawing 1, term  $R_{\min}$  means the reflectivity value in an about 14 thickness unit (chosen arbitrarily), light interference makes the minimal value of a reflectance versus thickness curve produce here --; --  $R_{\max}$  of this sample means the reflectivity value in an about 30 thickness unit, and light interference makes the maximal value of a reflectance versus thickness curve produce here A person skilled in the art measures reflectance by spectrophotometry.

[0012]The optical element by this invention is shown in (b) of drawing 2, and contains at least

three layers. The substrate 10 has the optical recording layer 12 and the reflecting layer 14 which have two sublayers on it. Although a protective layer may be used again, they are not explained therefore it is unnecessary to operation of this invention. The substrate 10 is transparent and the light which illuminates the optical recording layer 12 passes the substrate 10.

[0013]Record is attained by carrying out marking of the optical recording layer 12 by the write-in laser which focuses on the optical recording layer 12. The focusing laser beam heats the optical recording substrate 12 to the temperature beyond a room temperature substantially, and derives change in a medium. A similar change includes disassembly of the material which forms the gaseous substance which transforms the package of a medium in the form of a bubble, a void, or a pit, including condensation of the metallic component in a layer. The distortion with the material of the substrate 10 is caused again. The thing which has these change at least, or all the combination are returned by the reading laser beam which focused. Record consists of a mark of the comparatively low reflectance on the background of comparatively high reflectance about a reading laser beam thus.

[0014]The desirable example of this invention is an element of the compact disk (CD) which can be written in as shown in (b) of drawing 2. Reading and write-in laser are laser diode types, and, generally operate at 770 to 830 nm. Refer to the OpticalRecording (1990) of Allan B. Marchant for more perfect explanation of optical record and regeneration as well as the composition of a compact disk.

The substrate 10 substrate 10 is made from light transmittance state resin which carried out the surface treatment and as for which an end is not. Desirable resin to the example of (b) of drawing 2 is polycarbonate and polyacrylate. The substrate 10 includes the guide rail for laser tracking.

Any metal conventionally used as an optical recording material is possible for the reflecting layer 14 reflecting layer 14. useful metal -- vacuum deposition -- or sputtering is carried out and gold, silver, aluminum, copper, and those alloys are included. Gold is preferred as a material. Recording layer or optical recording layer 12 this invention uses the optical recording layer 12 given by the formula  $(\text{Te}_a \text{germanium}_b \text{C}_c \text{H}_d \text{O}_e)$ , a, b, c, d, and e are atomic ratios, and are  $> (c+d) 40$ ,  $d > 10$ ,  $a > 5$ ,  $b > 5$ ,  $e = 0$ , and  $a+b+c+d+e=100$  here, a reflecting layer and the optical recording layer 12 -- element  $R_{\min}$  or  $R_{\max}$  (element reflectance) -- about 780 nm -- about 70% -- or it is chosen so that more greatly.

[0015]The desirable manufacturing method of the optical recording layer 12 is DC sputtering. A desirable target contains both Te and germanium. A target is adjusted with melt casting or powder metallurgy art. The \*\* sputtering (co-sputtering) method is used alternatively, and, as for this, two or more sputtering targets in which a certain thing contains Te and a certain thing contains germanium are used. The atmosphere (atmosphere) must contain sputtering gas like

Ar or Kr, and hydrocarbon gas like methane. A useful layer is adjusted again using other gas like fluoride,  $H_2$ ,  $N_2$ , and  $NH_3$ , and it deals in it.

[0016]The layer containing germanium, Sb, Te, C, and H is manufactured for optical application (the Japan patent public presentation No. (1990) 171289 of Okawa, U.S. Pat. No. 4985349, European Patent application 0290009 (1988)). However, these layers were designed in order to use without a reflector for the optical recording layer 12. It is desirable to have a layer of high absorption to such application. For example, Okawa is indicating use of the layer made from  $Q < 35\%$ , and  $Q = CH_4 / (Ar + CH_4)$  is a rate of  $CH_4$  within sputtering gas here. It is indicated that a compound refractive index is about 3.7-0.59 i to the layer manufactured with either of the metal in the long list in which Okawa contains  $Q = 50\%$  and germanium, Te, and Sb by the European Patent application 0290009 (1988). The layer only gives 44.5% at only 5.6% of reflection, and the first interference maximum by the first interference minimum, when included in structure like drawing 2. These low reflectivity values are unsuitable to CD application. Even when there is more absorption, it is clear to CD application that the layer's made from lower Q value which was indicated by Okawa it is not more suitable. Drawing 4 of U.S. Pat. No. 4985349 indicates clearly that it is impossible to make a layer from content higher (C+H) than 40 atom % again, even when all sputtering atmosphere consists of  $CH_4$  (namely,  $Q = 100\%$ ). Therefore, it will be concluded that it is impossible to form the layer based on germanium, Te, Sb, C, and H which have a suitable optical constant for CD application, even when a person skilled in the art compares from these indications and a reflector is used.

[0017]As an ingredient not less than 40% of content (C+H) to a completely surprising thing germanium, It is not only manufactured using Te, but an optical property is obtained using a golden reflector and the layer thickness about the maximum of the beginning of an interference curve to the layer containing not less than 40% of (C+H) by using the structure where  $>70\%$  of reflection is expressed to drawing 2. the layer thickness concerning the minimum of the beginning of an interference curve when (C+H) is not less than 50% -- even using --  $>70\%$  of reflection is obtained. Such a layer of the above-mentioned structure of having a golden reflector in addition to suitable reflectance shows high recording sensitivity and contrast again. The sensitivity or contrast whose same layer is suitable when a reflector is not used could not be recorded on the other hand. These layers are considered to be unsuitable to the application to a monolayer optical recording medium.

[0018]Drawing 1 is a standard mixing plot which has the reflecting layer 14 in an optical element and which shows  $R_{max}$  and  $R_{min}$ , respectively. This plot has  $R_{max}$  and/or  $R_{min}$  equal to 70%, or satisfies the demand that it is larger than it. Sputtering of the target of germanium and Te is carried out to manufacture of the recording layer 12 within the atmosphere which consists of  $CH_4$  and/or other hydrocarbon. Alloy sputtering process is used again, when a

sputtering target comprises this element. Sputter deposition of the reflecting layer 14 is carried out within inactive gas environment. Target power, the rate of flow, and the pressure were controlled, while depositing the recording layer so that reflectance ( $> 70\%$ ) characteristic of CD might be attained.

[0019]The optical characteristic of these optical recording layers 12 was able to be adjusted so that it might be used on shorter wavelength. More important one found that the dependence to the wavelength of the optical characteristic was weak. It turned out that it has the suitable capability for high-density CD of the next generation demanded in order that these media may function in the range with a wide record laser wavelength. The structural abnormal conditions which completely met the thickness of the optical recording layer 12 unexpectedly produce write-in, notably high sensitivity. The above-mentioned improvement is attained by increasing the reactive gas rate of flow to a certain time in sputter deposition. Then, the improved optical recording layer 112 differs in the presentation on Au boundary from it in a substrate boundary. therefore -- the improved layer has at least two different sublayers -- it means that one adjoins a substrate and others adjoin a reflector boundary. These molds of a layer are called a sublayer (sublayer). The diffused junction (while the second deposition continues, reactive gas rate of flow increases gradually) sublayer operates like the junction (reactant gas flow increases before the second deposition) sublayer which clarified. Although this invention includes a sublayer or the bilayer effect, a multilayer or an inclination (graded) film is in the range of this invention again.

[0020]According to this invention, the recording sensitivity of the record element ((b) of drawing 2) which consists of sublayers is notably higher than that of the layer ((a) of drawing 2) thoroughly adjusted under the deposition conditions not changing more characteristic. The mold of the latter of an optical recording layer is called a single (single) layer or a standard layer for the purpose of explanation. As drawing 3 shows, this is the plot of the thickness of one optical recording layer of reflectance versus this invention, and the demand that it is more than whether  $R_{\max}$  and/or  $R_{\min}$  are equal to  $70\%$  and it is completely the same as it is shown by drawing 1.

[0021]The increase in the sensitivity by the bilayer effect is not beforehand discriminated from the value by which the optimum recording power (ORP) to a disk was measured. According to drawing 1 which is the plot of the thickness of the monolayer optical recording layer of one reflectance pair for which OPR depends not only on the original thermal property of an active layer but on the mechanical design of a disk, it is selectable in three structural designs of a record element. -- The all show the reflectance of  $70\%$ . By the recording layer thickness  $t_1$ , it seems to a disk that there is generally no sensitivity dramatically. This is promptly conducted by the reflector (layer of gold of typically high conductivity) which the laser energy absorbed by this film approached, and an active layer is a reason considered to prevent reaching a



temperature required for record. Although the layer thousands of Å thick adjoins the reflector, it does not participate in recording processing but is often called "the dead layer." Although the disk was recordable by the thickness  $t_2$  and  $t_3$ , the difference of the quantity of the possible thing which participates in recording processing showed experimentally that ORP was not the same. This calls the thickness effect.

[0022]The same reason is applied to the bilayer record element of the mold of (b) of drawing 2. % it realizes about drawing 3 which is the plot of thickness to reflectance versus a bilayer using the layer 12b of the thickness of the layers 12a and 40 of 70% of thickness (arbitrary units and the following -- the same) of  $R_{\min}$  23. The disk of reflectance is formed 70% again in the layer 12b of the thickness of the layers 12a and 40 of the thickness of 122.

[0023]If it summarizes, ORP of a disk which has the same reflectance does not need to be the same by possible composition, a presentation, and/or the thickness effect. However, when a certain restraint is given, ORP is used as a standard over comparison with the sublayer and monolayer record element about those true potentia or essential sensitivity. The conditions given are that each disk is 70% reflectance in either  $R_{\max}$  or  $R_{\min}$  position. This standard was chosen by the manufacturing process. The disk which has the thickness of the recording layer corresponding to a position is preferred when taking into consideration both the reliability of a manufacturing process, and a throughput.

[0024]Like the bilayer disk, a series of monolayer disks changed, reflectance was made from the circumference of the first minimum, and  $R_{\min}$  was about 70% reflectance here. ORP corresponding to reflectance was interpolated 70% from ORP by which this disk of a series of was measured, and % reflectance. To the monolayer disk, a series of reflectance kept other conditions of all the constant, changed assembly time, and was made, and some disks which have the thickness which changes by that cause although it is the same presentation were manufactured. A series of reflectance was formed by one or more methods to a series of sublayers.

[0025]Selection of a deposition parameter is dramatically restricted to a monolayer. For example, the partial pressure / the rate of flow, and assembly time of one  $\text{CH}_4$  realize 70%  $R_{\min}$  to a predetermined sputtering speed. Notably high flexibility exists to a bilayer, the 70% reflectance in the first minimum is many methods in each sublayer, namely, adjustment of \*\*, such as a thickness presentation and the  $\text{CH}_4$  rate of flow, can attain it.

[0026]The deposition parameter of some bilayer disks which comprised a series of reflectance specified as Table 1 as series #102 is shown. For example, disk #6 is prepared by \*\* sputtering of Te and germanium target using 12 and 52-W target power, respectively. The presentation of sputtering atmosphere becomes by adding  $\text{CH}_4$  gas to the Ar gas which flows

at the rate of 10 standard cubic centimeter (sccm) per minute by the pressure of 4.5mTorr. The sublayer 12a is deposited on the substrate 10 for 30 seconds at the partial pressure of  $\text{CH}_4$  of 1.38mTorr and 4sccm, and the rate of flow, respectively (see the (b) of drawing 2). The sublayer 12b was deposited on the 35-second intermediate layer 12a at the partial pressure of higher  $\text{CH}_4$  of 2.8mTorr and 9sccm, and the rate of flow, respectively. The sublayer 12b of a front 2 \*\* disk of the deposition parameter of disk #4 and disk #5 is the same as it of disk #6 except for the longer time done for period deposition. The reflecting layer 14 to all of these recording layers was an Au layer of the 800-A thickness by which sputtering was carried out within pure Ar. These disks can provide the protection lacquer overcoat of about 6-micrometer thickness again. These disks form a series of reflectance from which reflectance changes with the differences of 12b layer thickness.

[0027]The spectrum photometer was used in order to determine the reflectance of a disk at 780 nm. The reflectance of disk #4 is the minimum in a series, and it turned out that outline correspondence is carried out at  $R_{\min}$  position. The dynamic trait of each disk was determined as the linear velocity of 2.8 m/s using the automated in-house tester. ORP and reflectance which were determined such are shown in Table 1.

[0028]

[Table 1]

表 1

ディスク #	ターゲットワット数		Ar 流速及び圧力		CH <sub>4</sub> 流速		CH <sub>4</sub> 圧力 mTorr		堆積時間 sec		反射率	ORP
	Ge	Te	sccm	mTorr	層 12a	層 12b	層 12a	層 12b	層 12a	層 12b		
6	12	52	10	4.5	4	9	1.38	2.8	30	35	69.1	mW
4	12	52	10	4.5	4	9	1.38	2.8	30	50	65.6	10
5	12	52	10	4.5	4	9	1.38	2.8	30	70	68.1	7.5
												7

[0029] Table 2 shows the similar deposition parameter to the recording layer belonging to the series designed as series #115, and this is a monolayer of the lot prepared using the same target power as bilayer series #102. However, CH<sub>4</sub> partial pressure, the rate of flow, and assembly time were chosen so that the reflectance in R<sub>min</sub> to this series might be 70% of an

outline again. ORP of a disk and the reflectance of a disk are shown in Table 2 again.

[0030]

[Table 2]

表 2

ディスク ID	ターゲットウェット数		Ar 流速及び圧力		CH4 流速及び圧力		堆積時間	反射率	ORP
	Gθ	Tθ	sccm	mT	sccm	mT			
14	52	12	10	4.5	5.5	1.79	70	79.9	20
15	52	12	10	4.5	5.5	1.79	90	67.9	10
16	52	12	10	4.5	5.5	1.79	110	71	10

[0031] ORP to reflectance and % reflectance of the two above-mentioned series are plotted by drawing 4 again. -- The circle to which an extraction circle includes a point in series #115 (monolayer) shows series #102 (bilayer). The circle of each group is connected by the dashed line which has an arrow which shows the direction of the increase in thickness. These lines express the relation of ORP versus the reflectance from the first minimum as which ORP is

determined. ORP which the reflectance in the first minimum is 65.5%, and corresponds to this sublayer series is 7.5 mW. The reflectance in the first minimum to monolayer series is 66.8%, and corresponding ORP is 7.5 mW. A sublayer may be more highly sensitive than a monolayer and lower power may be sufficient as the former to writing. However, small amendment is required in order to calculate a difference with those small reflectance.

[0032]The approximate relation has been experientially determined between reflectance and ORP to one of the conditions. This is shown in drawing 4 as the sensitivity reference line C. ORP in reflectance is projected on 10.5 mW to a 8.7-mW monolayer to a bilayer medium using this line 70% to the first minimum. The bilayer recording disk in the above-mentioned example has sensitivity higher than -1.8mW from a monolayer. Under other existing processing conditions, even if the improvement in the sensitivity by bilayer multilayer structure assumes that it can become larger than 1.8 mW, it is appropriate. It is because the 70% reflectance in the position of the first minimum is obtained by adjustment of \*\*, such as a way, for example, sublayer thickness, many differ, and a presentation.

[0033]Although this invention has been explained in detail with reference to the specific desirable example of that, change and improvement are effective at the pneuma of this invention, and within the limits.

[0034]

[Effect of the Invention]A presentation and thickness of an optical recording layer and a reflecting layer can be superior to the monolayer disk of  $R_{\min}$  reflectance with same recording sensitivity to an element. A presentation and thickness of an optical recording layer and a reflecting layer can be superior to the monolayer disk of  $R_{\max}$  reflectance with same recording sensitivity to an element.

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[Translation done.]

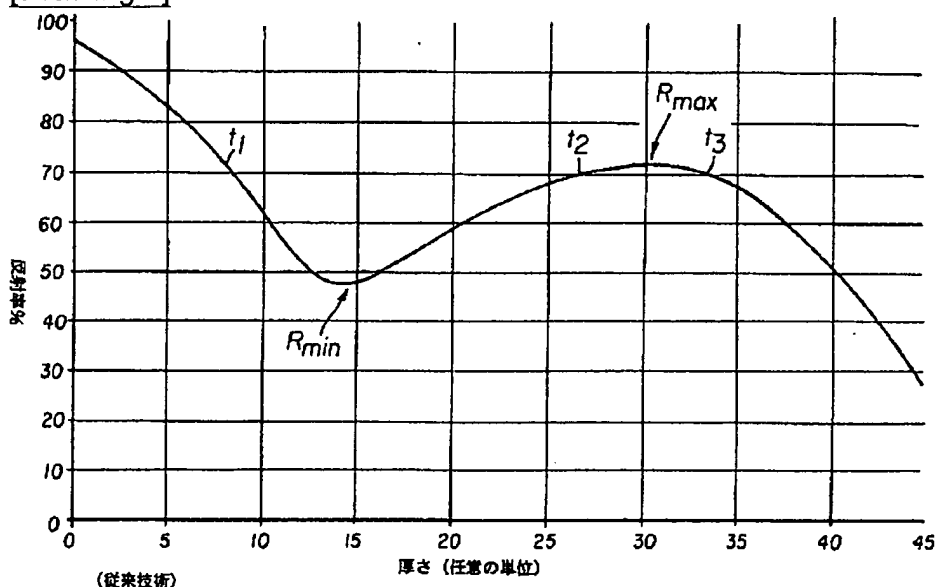
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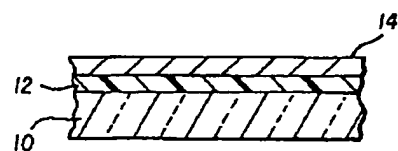
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## DRAWINGS

[Drawing 1]

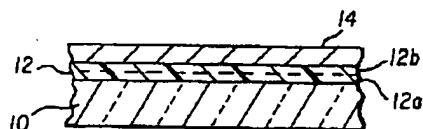


[Drawing 2]



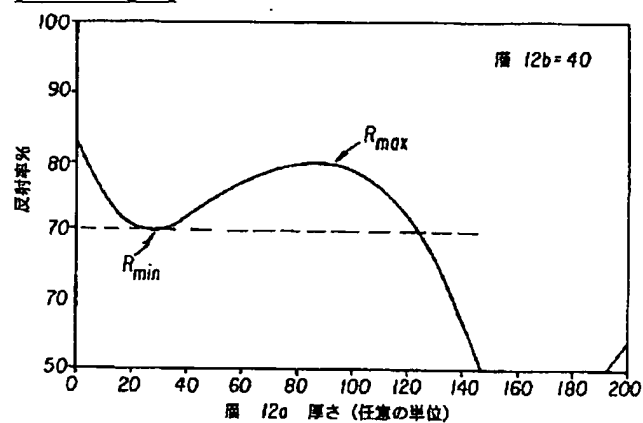
(a)

(従来技術)

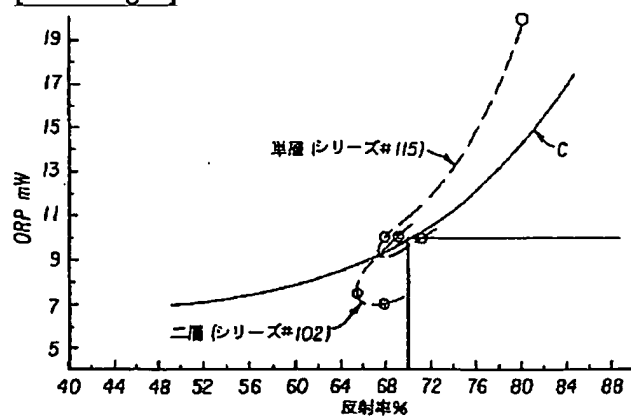


(b)

[Drawing 3]



[Drawing 4]



[Translation done.]